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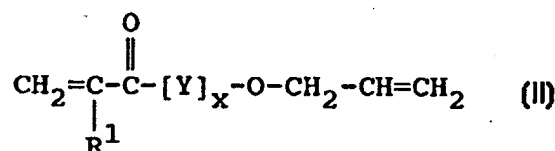
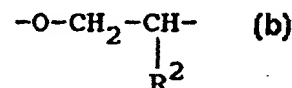
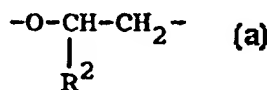
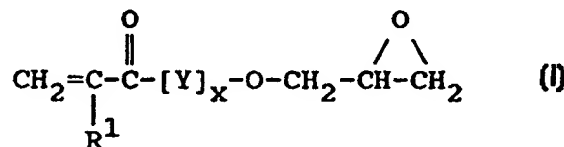
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: <b>PCT/EP97/07283</b></p> <p>(22) International Filing Date: <b>22 December 1997 (22.12.97)</b></p> <p>(30) Priority Data: <b>08/772,979</b>      <b>23 December 1996 (23.12.96)</b>      <b>US</b></p> <p>(71) Applicant (for all designated States except PL US): <b>SAR-TOMER COMPANY, INC. [US/US]; Oaklands Corporate Center, 502 Thomas Jones Way, Exton, PA 19341 (US).</b></p> <p>(71) Applicant (for PL only): <b>CRAY VALLEY S.A. [FR/FR]; Tour Total, 24, cours Michelet, F-92800 Puteaux (FR).</b></p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): <b>FAN, Mingxin [CN/US]; 49 Sheffield Lane, West Chester, PA 19380 (US). CESKA, Gary, W. [US/US]; 310 Long Ridge Lane, Exton, PA 19341 (US). HORGAN, James [US/US]; 805 Copeland School Road, West Chester, PA 19380 (US). HAZELL, Thomas, W. [US/US]; 233 Lindenwood Drive, Exton, PA 19341 (US).</b></p> <p>(74) Agent: <b>CHAILLOT, Geneviève; Cabinet Chaillot, 16-20, avenue de l'Agent Sarre, Boîte postale 74, F-92703 Colombes Cedex (FR).</b></p>	<p>(81) Designated States: <b>CA, CN, JP, KR, MX, PL, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b></p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	

(54) Title: **ALKOXYLATED GLYCIDYL (METH)ACRYLATES AND METHOD OF PREPARATION**

## (57) Abstract

The present invention relates to compounds of formula (I) ( $R^1 = H, CH_3$ ; each of the Y, which may be the same or different when x is higher than 1, represents an alkylene oxide unit of formula (a) or (b), wherein  $R^2$  is hydrogen or  $(C_1-C_6)$  alkyl; and  $x = 1-20$ , with the proviso that x is higher than 10 when all the alkylene oxide units Y are ethylene oxide units); and to a process for preparing compounds (I) which comprises reacting an alkoxyalted allyl acrylate or methacrylate of formula (II) wherein  $R^1$  and Y are as defined above and  $x = 1-20$ , with hydrogen peroxide in the presence of (a) tungstic acid or a metal salt thereof or molybdic acid or a molybdenum oxide; (b) phosphoric acid or a metal salt thereof; and (c) at least one phase transfer catalyst.



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ALKOXYLATED GLYCIDYL (METH)ACRYLATES AND METHOD OF PREPARATION.

This invention relates to a new class of acrylates and methacrylates, hereinafter "(meth)acrylates", containing epoxide functionalities and methods for their preparation.

Glycidyl (meth)acrylate, having two different polymerizable functional groups, is widely used as a chemical intermediate. The (meth)acrylate group can be polymerized or copolymerized into a polymer backbone while the epoxide functional group is kept intact which then can be further modified. Currently, glycidyl methacrylate is produced from epichlorohydrin and sodium methacrylate salt. Sodium chloride is generated as by-product which is contaminated with epichlorohydrin. Epichlorohydrin is a very toxic material, and most working places are not equipped to handle it. Epichlorohydrin is present in the final glycidyl (meth)acrylate product even after normal purification. Glycidyl methacrylate itself has a low boiling point and is fairly volatile and toxic.

Epoxidation of unsaturated organic compounds has been known for sometime to generate epoxide groups. Olefins can be epoxidized with a number of peracids and peroxides, such as trifluoroperacetic acid (J. Am. Chem. Soc. 1955, 77, 89) and t-butyl peroxide (J. Am. Chem. Soc. 1980, 102, 5974).

Hydrogen peroxide is a very attractive and economical oxidant industrially since the only by-product generated is water. Epoxidation using hydrogen peroxide in the presence of metal catalysts has been known for some time. U.S. Patent 2,833,787 and 2,833,788 describe the epoxidation of unsaturated alcohol with hydrogen peroxide and sodium tungstate. Unsaturated acids have been epoxidized using hydrogen peroxide and sodium tungstate. (J. Org. Chem. Vol. 52, 1868 and Vol. 53, 3582). Molybdenum and hydrogen peroxide have also been used for the peroxidation of olefins (Angew. Chem. Int. Ed. Engl. 1982, 21, 734-750). Under phase transfer catalysis conditions, water soluble alkali metal

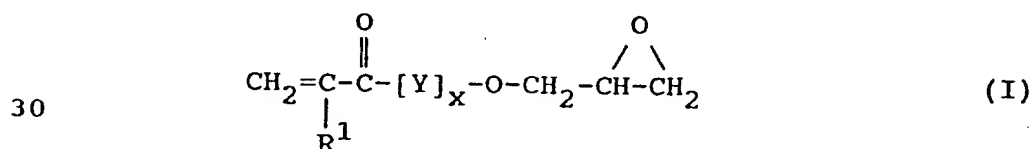
tungstate and hydrogen peroxide have been used to epoxidize olefins in the presence of excess of olefins (J. Org. Chem. 1985, 50, 2688-2690). Heteropolyacids have been also used in combination of hydrogen peroxide to epoxidize olefins  
 5 (J. Org. Chem. 1987, 52, 1868-1870 ; J. Org. Chem. 1988, 53, 3587-3593).

Epoxidation of vinyl norbornene (meth)acrylate at 50°C using peracetic acid has been reported (US 3,459,775) ; the final yield is very low and normally less than 42%.  
 10 Japanese patent application JP-A-62/81 378 describes the epoxidation of dicyclopentenylxyethyl acrylate at 60°C using 35% hydrogen peroxide with less than 48% yield.

U.S. Patents 5,283,360 and 5,510,516 to Caubere, et al, show epoxidation of unsaturated (meth)acrylate esters  
 15 with hydrogen peroxide using a catalyst system which comprises alkali metal salts of tungstic or molybdinic acids and a heteropolyacid. Caubere et al do not show (meth)acrylates which have been alkoxyated, nor do they show phosphoric acid.

20 GB application 2 055 821 A by Venturello, et al, shows epoxidation of olefins with hydrogen peroxide using a catalyst system consisting of W, Mo, or V, and at least one derivative of P or As. This application does not show epoxidation of (meth)acrylates or alkoxyated compounds.

25 This invention relates to a new class of (meth)acrylate monomers of the formula :



wherein :

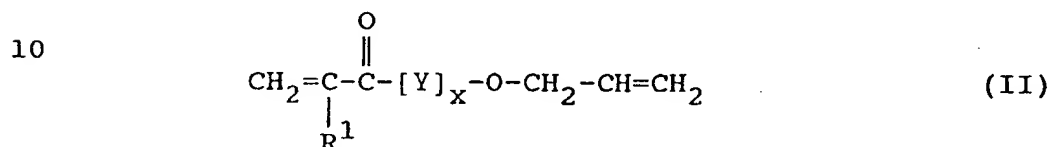
- $\text{R}^1 = \text{H}, \text{CH}_3$  ;
- each of the Y, which may be the same or different when  
 35 x is higher than 1, represents an alkylene oxide unit of the formula  $-\text{O}-\underset{\text{R}^2}{\text{CH}}-\text{CH}_2-$  or  $-\text{O}-\text{CH}_2-\underset{\text{R}^2}{\text{CH}}-$ , wherein  $\text{R}^2$  is

hydrogen or (C<sub>1</sub>-C<sub>6</sub>) alkyl ; and

- x = 1-20, with the proviso that x is higher than 10 when all the alkylene oxide units Y are ethylene oxide units.

In particular, in the formula (I), R<sup>1</sup> = CH<sub>3</sub>, the Y units are propylene oxide units and x = 1-20, especially 2-5.

This invention also comprises a process for preparing such compounds by reacting a compound of the formula :



wherein R<sup>1</sup> and Y are as defined above and x = 1-20,  
15 with hydrogen peroxide in the presence of :

- (a) tungstic acid or a metal salt thereof or molybdic acid or a molybdenum oxide ;
- (b) phosphoric acid or a metal salt thereof ; and
- (c) at least one phase transfer catalyst.

20 The compounds of the invention are useful as monomers, and are glycidyl (meth)acrylate derivatives with higher molecular weight than glycidyl (meth)acrylate. They have utility as chemical intermediates where the additional polyether group is advantageous.

25 An advantage of the process of the invention for the preparation of the monomers is that it does not involve epichlorohydrin which is very toxic. The process involves only a low level of catalyst composition and no organic and/or peracid, which results in simple product workup and  
30 process. The new catalyst composition is highly effective and efficient. The epoxidation of the alkoxyated allyl (meth)acrylate compounds of formula (II) is carried out with hydrogen peroxide in the presence of tungstic acid or its metal salts, or molybdic acid or a molybdenum oxide,  
35 phosphoric acid or its metal salts, and phase transfer catalyst, and can be performed at any temperature which is sufficient to react, however, particularly suitable

temperatures are between 0°C and 100°C, preferably from 25°C to 70°C and more particularly from 50 to 70°C. The reaction takes place faster at higher temperature and requires shorter time to complete. The reaction is typically exothermic and  
5 slow addition of hydrogen peroxide is preferred to control the exotherm. At higher temperature hydrogen peroxide undergoes decomposition. The reaction can be performed at pressures from subatmospheric to superatmospheric pressures ; however, the reaction is preferably carried out at  
10 atmospheric pressure.

The compounds of formula (II) can be prepared according to known methods, for example the method shown in U.S. Pat. 4,618,703 to Ceska.

The epoxidation can be performed with or without  
15 solvent, but solvent is preferred to reduce the viscosity. Suitable solvents are water-immiscible organic solvent such as chlorinated hydrocarbons, ethers, glycol ethers, hydrocarbons, alkyl esters or combinations thereof can be used. Particular suitable organic solvents are toluene,  
20 chlorobenzene, chloroform, methylene chloride, heptane and the like.

Hydrogen peroxide solution is used as oxidant in the concentration in water of about 5 to 70% by weight. The amount of hydrogen peroxide can vary depending on the desired  
25 degree of epoxidation, typically from 0.1 to 1.5 equivalent and preferably from 1.0 to 1.5 equivalent per equivalent of carbon-carbon allylic double bond in the compound of formula (II).

The phase transfer catalyst can be used from 0.001  
30 to 1, preferably 0.05 to 0.1, equivalent per equivalent of carbon-carbon allylic double bond in the compound of formula (II). Suitable phase transfer catalysts include quaternary ammonium salts, quaternary phosphonium salts, polyethers, and polyether derivatives such as polycondensates  
35 of polyethers or functional polyethers, and the like. Examples of phase transfer catalysts include, for example,

trioctylmethylammonium chloride, trioctylmethylammonium bromide, trioctylmethylammonium iodide, trioctylmethylammonium hydrogen sulfate, trioctylmethylammonium nitrate, tetrahexylammonium chloride, tetrahexylammonium bromide, 5 tetrahexylammonium iodide, tetrahexylammonium hydrogen sulfate, tetrahexylammonium nitrate, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium nitrate, tetrabutylammonium hydrogen sulfate, dioctadecyldimethylammonium chloride, dioctadecyldimethyl- 10 ammonium bromide, dioctadecyldimethylammonium nitrate, dioctadecyldimethylammonium hydrogen sulfate, dihexadecyldimethylammonium chloride, dihexadecyldimethylammonium bromide, dihexadecyldimethylammonium nitrate, dihexadecyldimethylammonium hydrogen sulfate, 15 trioctylmethylphosphonium chloride, trioctylmethylphosphonium bromide, trioctylmethylphosphonium nitrate, trioctylmethylphosphonium hydrogen sulfate, tetrahexylphosphonium chloride, tetrahexylphosphonium bromide, tetrahexylphosphonium nitrate, tetrahexylphosphonium hydrogen sulfate, tetrabutylphosphonium 20 chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium nitrate, tetrabutylphosphonium hydrogen sulfate, tetrabutylphosphonium iodide, dioctadecyldimethylphosphonium chloride, dioctadecyldimethylphosphonium bromide, dioctadecyldimethylphosphonium nitrate, dioctadecyldimethyl- 25 phosphonium hydrogen sulfate, dihexadecyldimethylphosphonium chloride, dihexadecyldimethylphosphonium bromide, dihexadecyldimethylphosphonium nitrate, dihexadecyldimethylphosphonium hydrogen sulfate, tetraalkylammonium hydroxide, tetraalkylammonium tribromide, tetraalkylammonium trifluoro- 30 methanesulfonate, and any combination thereof.

Phosphoric acid or its various salts can be used from 0.001 to 1, preferably 0.05 to 0.1, equivalent per equivalent of carbon-carbon allylic double bond in the compound of formula (II). Sodium or potassium monobasic, 35 dibasic, or tribasic salts of phosphoric acid can also be used. The final pH can be adjusted by other acids or bases to a value between 0 and 5.



Tungstic acid or its metal salts or molybdic acid or molybdenum oxide can be used as the metal catalysts. The metal salts of tungstic acid are water soluble and the tungstic acid is not. The typical amount of metal catalyst 5 is used from 0.005 to 5%, preferably about 0.1 to 1%, based on compound of formula (II). The preferred catalyst is tungstic acid - which is not water soluble ; molybdic acid is another preferred catalyst.

Furthermore, the reaction according to the present 10 invention can be made advantageously in the presence of a polymerization inhibitor, such as 4-methoxyphenol.

The epoxidized unsaturated (meth)acrylates can be used in a curable or polymerizable composition in a variety of applications, such as coatings, epoxy/amine cure, cationic 15 cure/free radical hybrid cure, and as chemical intermediates for polymers.

The following non-limiting examples are presented to illustrate a few embodiments of the invention. All parts and percentages are by weight unless otherwise indicated.

20

#### EXAMPLE 1

##### Synthesis of Propoxylated Allyl Methacrylate (5 PO) of Formula (II)

Propoxylated allyl alcohol (5 propylene oxide units per molecule) (1344.8 g), methacrylic acid (448.5 g), 25 4-methoxyphenol (6.75 g), methanesulfonic acid (70%, 33.75 g) and heptane (405.0 g) were added to a reactor and stirred at room temperature, with air sparge being applied. The mixture was heated to reflux while water generated was removed via azeotrope. After the reaction was complete (no more water 30 formation) the mixture was neutralized with 25% NaOH and washed twice with 25% NaOH. The final product, propoxylated allyl methacrylate, was obtained by removing the heptane solvent under reduced pressure. Yield was 1532.4 grams.

EXAMPLE 2Synthesis of propoxylated allyl methacrylate (2 PO) of Formula (II)

Example 1 was repeated using 2 PO allyl alcohol.  
5 Allyl methacrylate having 2 propylene oxide groups per molecule was obtained.

EXAMPLE 3Epoxidation of propoxylated allyl methacrylate (5 PO)

100.0 g unsaturated propoxylated allyl methacrylate  
10 ester from Example 1 was dissolved into 100.0 g toluene.  
Then, 2.7 g  $(\text{MeN}[(\text{CH}_2)_7\text{CH}_3]_3)_3 (\text{PO}_4[\text{WO}(\text{O}_2)_2]_4)$  was added to the solution. The solution was stirred and heated to 60°C followed by slow addition of 50.0 ml  $\text{H}_2\text{O}_2$  (30%) in 30 min. After 22.0 hours, the reaction mixture was analyzed by GC,  
15 which showed 85% conversion to epoxide.

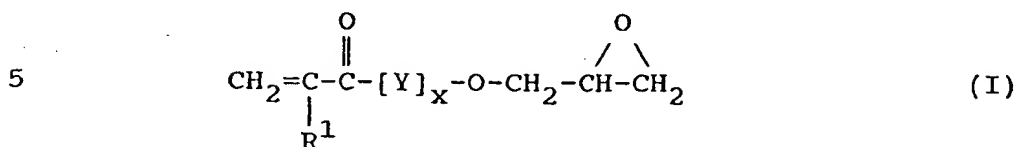
EXAMPLE 4Epoxidation of propoxylated allyl methacrylate (5 PO)

3.0 g  $\text{H}_2\text{WO}_4$ , 1.5 g NaOH (25%) and 1.5 g  $\text{H}_3\text{PO}_4$  (85%)  
were added to a reactor at room temperature. Then 200.0 g  
20 propoxylated allyl methacrylate (5 PO) ester produced according to Example 1, 200.0 g toluene, and 3.0 g trioctyl methyl ammonium chloride were added. The mixture was stirred and heated to 60°C for 23 hours. GC analysis showed complete epoxidation to propoxylated glycidyl methacrylate.

25 While the invention has been described in sufficient detail for those skilled in the art to make and use it, various modifications, alternatives, and improvements should become readily apparent without departing from the spirit and scope of the invention as set forth in the  
30 following claims.

## CLAIMS

1 - (Meth)acrylate compounds of the the formula :



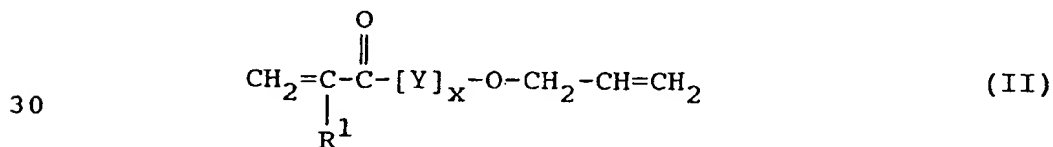
wherein :

- $R^1 = H, CH_3$  ;
- 10 - each of the Y, which may be the same or different when x is higher than 1, represents an alkylene oxide unit of the formula  $-O-\underset{\underset{|}{R^2}}{CH}-CH_2-$  or  $-O-CH_2-\underset{\underset{|}{R^2}}{CH}-$ , wherein  $R^2$  is
- 15 hydrogen or  $(C_1-C_6)$  alkyl ; and
- $x = 1-20$ , with the proviso that x is higher than 10 when all the alkylene oxide units Y are ethylene oxyde units.

2 - Compounds according to claim 1, characterized by the fact that  $R^1 = CH_3$ , the Y units are propylene oxide 20 units and  $x = 1-20$ .

3 - Compounds according to claim 2, characterized by the fact that  $x = 2-5$ .

4 - Process for preparing compounds as defined in anyone of claims 1 to 3, characterized by the fact that it comprises reacting an alkoxyated allyl acrylate or methacrylate of formula :



wherein  $R^1$  and Y are as defined in claim 1 and  $x = 1-20$ , with hydrogen peroxide in the presence of :

- 35 (a) tungstic acid or a metal salt thereof or molybdic acid  
or a molybdenum oxide ;  
(b) phosphoric acid or a metal salt thereof ; and  
(c) at least one phase transfer catalyst.

5 - Process according to claim 4, characterized by the fact that said hydrogen peroxide is introduced in an amount of about 0.1 to 1.5 equivalent, in particular of about 1.0 to 1.5 equivalent, per equivalent of carbon-carbon allylic double bond in the compound of formula (II).

6 - Process according to anyone of claims 4 and 5, characterized by the fact that the reaction is conducted at a temperature of about 0°C to 100°C.

7 - Process according to claim 6, characterized by the fact that the reaction is conducted at a temperature of about 25°C to 70°C, particularly at a temperature of about 50°C to 70°C.

8 - Process according to anyone of claims 4 to 7, characterized by the fact that the phase transfer catalyst is present in an amount of about 0.001 to 1 equivalent, in particular of about 0.05 to 0.1 equivalent, per equivalent of carbon-carbon allylic double bond in the compound of formula (II).

9 - Process according to anyone of claim 4 to 8, characterized by the fact that the phase transfer catalyst is selected from the group consisting of quaternary ammonium salts, quaternary phosphonium salts, polyethers and polyether derivatives.

10 - Process according to anyone of claims 4 to 9, characterized by the fact that the reaction is conducted in the presence of a water-immiscible organic solvent.

11 - Process according to claim 10, characterized by the fact that the water-immiscible organic solvent is selected from the group consisting of chlorinated hydrocarbons, ethers, glycol ethers, hydrocarbons, alkyl esters and combinations thereof, in particular from the group consisting of toluene, chlorobenzene, chloroform, methylene chloride and heptane.

12 - Process according to anyone of claims 4 to 11, characterized by the fact that the phosphoric acid or phosphoric acid salt comprises about 0.001 to 1 equivalent

per equivalent of carbon-carbon allylic double bond in the compound of formula (II).

13 - Process according to anyone of claims 4 to 12, characterized by the fact that the phosphoric acid salt is a sodium or potassium monobasic, dibasic, or tribasic phosphoric acid salt.

14 - Process according to anyone of claims 4 to 13, characterized by the fact that the pH of the reaction is adjusted by acids or bases at a value between 0 and 5.

10 15 - Process according to anyone of claims 4 to 14, characterized by the fact that the tungstic acid or salts thereof or molybdic acid or molybdenum oxide is present in an amount of about 0.005 to 5% based on weight of compound of formula (II).

15 16 - Process according to anyone of claims 4 to 15, characterized by the fact that it is conducted in the presence of a polymerization inhibitor.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/07283

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D303/16 C07D303/24 C07D301/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 510 516 A (CAUBERE ET. AL.) 23 April 1996 cited in the application see column 2, line 13 - column 3, line 29 see column 4, line 64 - column 5, line 35; claims ---	1-16
Y	EP 0 741 134 A (ENICHEM ) 6 November 1996 see whole document ---	1-16
Y	GB 2 055 821 A (ISTITUTO GUIDO DONEGANI) 11 March 1981 cited in the application see claims; examples ---	1-16
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Patent family members are listed in annex.

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Date of the actual completion of the international search

30 April 1998

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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